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### Abstract:

The variation of the Si-O bonds population in the oxynitride films deposited on Si has been found by IR spectroscopy after post thermal annealing at 1050/spl deg/C for t/sup 2/. The Si-O bonding in SiON film has been related to a sequences of two processes indicated by the time dependency of the integral absorption band of the asymmetric Si-O stretching vibration mode at 1075 cm/sup -1/. We have found a fast increase of the Si-O bonds population after about 45 min of heating. The time dependency shows an almost linear dependence versus t/sup 1/2/. The break of the slope is produced only after a second preliminary low rate increase process in Si-O bonding roughly speaking being much smaller than in the second process. The annealing behavior of both, the real and imaginary part of the refractive index  $n^*(\lambda) = n(\lambda) + ik(\lambda)$  has been extracted using UV-VIS spectra simulation. The result indicates a systematic decrease of n and k with the heating time at 1050/spl deg/C in SiON films, suggesting the increasing of oxygen content in SiON films.

### Index Terms:

dielectric thin films silicon compounds CVD coatings annealing bonds (chemical) spectra ultraviolet spectra visible spectra refractive index structure LPCVD silicon nitride film wet oxygen Si-O bond population IR spectroscopy thermal annealing vibration mode absorption band refractive index UV-VIS spectra 1050 C SiON

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# STRUCTURE CHANGES IN LPCVD SILICON OXYNITRIDE FILMS INDUCED BY ANNEALING IN WET OXYGEN

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**Abstract.**—The variation of the Si-O bonds population in the oxynitride films deposited on c-Si has been found by IR spectroscopy after post thermal annealing at 1050°C in wet O<sub>2</sub>. The Si-O bonding in SiON film has been related to a sequences of two steps, indicated by the time dependency of the integral absorption band of the asymmetric stretching vibration mode at 1075cm<sup>-1</sup>. We have found a fast increase of Si-O population after about 45min of heating. The time dependency shows an almost linear dependence versus  $t^{1/2}$ . The break of the slope is produced only after a preliminary low rate increase process in Si-O bonding roughly speaking being 21 times smaller than in the second process. The annealing behavior of both, the real and the imaginary part of the refractive index  $n^*(\lambda) = n(\lambda) + ik(\lambda)$  has been extracted using UV-VIS spectra simulation. The result indicates a systematic decrease of  $n$  and  $k$  with the heating time at 1050°C in wet O<sub>2</sub>, suggesting the increasing of oxygen content in SiON films.

## I. INTRODUCTION

The quality of SiON films is of great importance especially for microelectronics ULSI MOS applications as an alternative for the silicon oxide gate dielectric. The ratio O/N+O in the films determines the electric, optical and mechanical properties while the concentration of Si-H bonds influences the trapping properties of the film and thus the electrical stability of MOS devices [1], [2], [3].

Within this paper we investigate the role of post deposition annealing in wet O<sub>2</sub> at 1050°C on the composition properties of LPCVD SiON films, by means of infrared IR and UV-VIS spectroscopy. Earlier experience has revealed favorable effects in releasing the stress of silicon nitride layers by annealing in wet oxygen [4], related to silicon etching technology through a Si<sub>3</sub>N<sub>4</sub> mask. Actually, the efficiency of low temperature CVD SiO<sub>2</sub> films annealing in wet oxygen on increasing breakdown characteristics, has been already demonstrated [5]. The stability of SiON films exposed in wet oxygen at 1050°C was investigated relative to solid state chemical reaction of oxygen and related to Si-O network build up in the

LPCVD oxynitride film which has a glassy structure in its "as deposited" state. The evolution of the Si-O bonds population in SiON films versus annealing time has been estimated by monitoring the asymmetrical stretching mode vibration at 1075 cm<sup>-1</sup>. Global properties determined by chemical changes in SiON films are studied by UV-VIS spectroscopy. The complex refractive index has been extracted from UV-VIS data by fitting the experimental spectra with the simulated ones.

## II. EXPERIMENTAL CONDITIONS AND METHODS

The preparation of the LPCVD SiON films has been performed in horizontal hot wall ASM reactor provided with quartz heated by electrical resistance. LPCVD silicon oxynitride thin films were deposited on 3-inch (100) p-type silicon wafers using a mixture of SiCl<sub>2</sub>H<sub>2</sub>-NH<sub>3</sub>-N<sub>2</sub>O at 860°C and 400 mTorr. We have prepared SiON samples, at a relative gas flow ratio  $r = Q_{N_2O}/Q_{NH_3}$  equal with 7. Details about the deposition of the LPCVD SiON layers are presented in a previous paper [3]. Preliminary optical measurements of the refractive index were performed for as deposited SiON films at  $\lambda = 632.8\text{nm}$ . The as-deposited films were isothermally treated in O<sub>2</sub> and H<sub>2</sub>O vapors in an open quartz tube at a temperature of 1050°C for different periods of time from 30 to 120 minutes. Infrared spectroscopy has been used to identify structural changes in SiON produced by post growth high temperature annealing. IR measurements have been performed using FT-IR Perkin Elmer spectrometers. The relation between local structure changes and macroscopic properties (as refractive index and extinction coefficient) has been investigated by using an approach based on optical parameter extraction from UV-Vis spectra. This approach fits the experimental data by simulating UV-VIS spectra in the frame of the well known multiple layer model based on matrix algorithm, briefly

described in the section 3.3. UV-VIS measurements have been done by using SPECORD M-40 type spectrometer. UV-VIS reflection spectra were measured in absorbency mode, in order to obtain a very sharp peaks, and thus to improve the fitting accuracy of the experimental data in respect with the theoretical calculated spectra.

### III. CHARACTERIZATION OF SiON FILMS ANNEALED IN WET OXYGEN

The annealing of the as-deposited LPCVD SiON films in wet O<sub>2</sub> has been investigated in relation with the changes of the chemical structure. The main result is given in Fig.1a, meaning the generation of the Si-O bonds which are revealed by the absorption band at 1075 cm<sup>-1</sup> [6].

The integral intensity of the asymmetric stretching vibration of Si-O-Si band increases systematically versus annealing time. This is a clear indication of the gradual increase of the Si-O population network inside the glassy structure of the silicon oxynitride film. This annealing behavior of the SiON is mainly determined by physical-chemical processes activated by high temperature and wet oxygen ambient. The absence of the separate absorption bands in as deposited sample suggests that this material has a glassy structure with no distinct SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> phases [7], [8]. In order to understand the mechanism of the oxygen bonding inside the annealed SiON film induced at 1050°C in wet O<sub>2</sub>, we present in Fig.1b the integral intensity of the absorption band at 1075 cm<sup>-1</sup> versus  $\sqrt{t}$ , where  $t$  is the heating time.

The experimental data for annealing time longer than about 45 minutes indicate a tendency to a linear dependency with  $\sqrt{t}$ . The meaning of this feature is that for long heating times the increase in Si-O bond population is a diffusion-limited chemical process.

The data shown in Fig.1b indicate at least two different processes of Si-O bond formation at 1050°C in wet O<sub>2</sub>. During the early stage of annealing the amount of Si-O bonds increases slowly at a lower rate than during the diffusion-limited chemical process. Roughly speaking the break after 45 minutes of heating in wet O<sub>2</sub> turns the average initial slope to a value of about 21 times greater than during the previous stage.

We expect that the OH groups coming at high temperature from wet ambient diffuse into the

initial SiON matrix and may break the silicon bonds of the above tetraedra and thus Si-OH groups are formed. Then, two such Si-OH groups may react together (condensation reaction) and provide a Si-O-Si bond, releasing a water molecule.

Other possible condensation reactions Si-OH + Si-H) can take place and thus release hydrogen molecular species. These temperature-assisted interactions can explain both the Si-O-Si formation and the decrease in H content by the ex-diffusion of the resulted water.

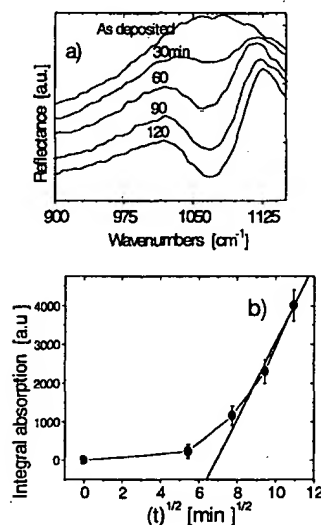


Fig. 1. a) Si-O-Si asymmetric stretching mode of the annealed SiON film in wet O<sub>2</sub> at 1050°C for 30, 60, 90 and 120 min. The as-deposited oxynitride film has a thickness of 1140 nm and  $n = 1.67$  at a wavelength of 600 nm. b) The dependence of the Si-O-Si integral absorption band at 1075 cm<sup>-1</sup> versus  $\sqrt{t}$ , where  $t$  is annealing time at 1050°C.

Moreover, this increased number of Si-O-Si bonds accelerates the diffusion of new OH species coming from a hot and wet ambient, and thus an increased slope in the formation of Si-O-Si bonds at longer times, found experimentally can be easier understood..

### IV. OPTICAL PARAMETER EXTRACTION BASED ON THEORETICAL CALCULATION OF UV-VIS SPECTRA

The theory of light propagation in non-homogeneous media based on matrix formalism [9]–[10] has been used to simulate optical spectra of oxynitride or Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> multiple layer structures, in the range of 190–700 nm.

The thickness of the sample to be investigated is considered as an ensemble of very thin layers.

They are taken as parallel plates whose thickness is very small compared with the wave length of the incident light ( $d/\lambda \ll 1$ ). The refractive index is expressed as a complex number  $n^* = n + ik$  with  $n$  and  $k$  depending on the light wavelength. The theory of UV-VIS simulation spectra takes into account the potential dependence of  $n^*(\lambda)$  as a function of depth [10]–[11]. The explicit depth dependency of  $n^*(x, \lambda)$  for non-homogeneous films can be extracted by a more complex fitting procedure. In this study it is assumed that refractive index has the same value along the whole thickness of the SiON films. The relation between incident, transmitted and reflected amplitudes is given by a complex matrix related to each thin plate considered in the physical model. The total effect of the oxynitride film is given by matrix multiplication.

The theoretic spectra are fitted to experimental data processed by a PC using the A/D interfaced spectrometer. The extraction of  $n(\lambda)$  and  $k(\lambda)$  from UV-VIS spectra is based on a specific approach which takes into account the light propagation features in a thin film sample deposited on c-Si. The method gives good results for films thickness greater than the value corresponding to the first color order. The wave length dependency of the refractive index is considered to be approximated by a Sellmeier's function:

$$n(\lambda) = \sqrt{1 + \frac{(A^2 - 1)}{1 - \left(\frac{B}{\lambda}\right)^2}}; \quad k(\lambda) = D \exp\left(-\frac{\lambda - \lambda_0}{f}\right)$$

where  $\lambda_0 = 190$  nm.

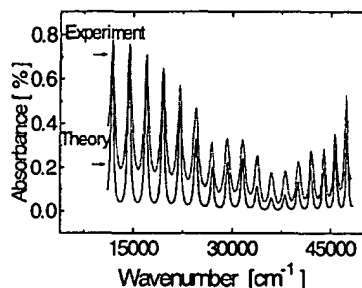


Fig. 2. Experimental and calculated spectra resulted from the fitting procedure for UV-VIS spectra of the as deposited SiON sample  $n = 1.67$ ,  $g = 1140$  nm

The extinction coefficient function  $k(\lambda)$  from the above equation has been approximated by an exponential decay [12]. The fitting procedure starts with the long wave domain (600–900 nm) using only two parameters  $A$  and  $B$  belonging to the equation given in (1). The starting value for the film thickness measured from ellipsometry is taken as an input data.

The error is considered in respect with the wavelength of the local reflectance extreme values. Fig.2 shows the experimental UV-Vis spectra for an as-deposited silicon oxynitride film ( $n = 1.67$ ) and the theoretical spectra resulted from the fitting procedure. The spectrometer has been used for reflection spectra recording in the absorbency mode, for which a sharp maxima have been obtained. It gives the best condition for an accurate fit. In Fig.3.a and Fig.3.b the extracted  $n(\lambda)$  and  $k(\lambda)$  functions from experimental UV-VIS spectra are shown. The refractive index decreases as a result of the Si-O bonding in tetrahedra from 1.673 to 1.642 after an hour and to 1.623 after two hours at 1050°C in wet oxygen. These values are considered at a wavelength of 623.8 nm.

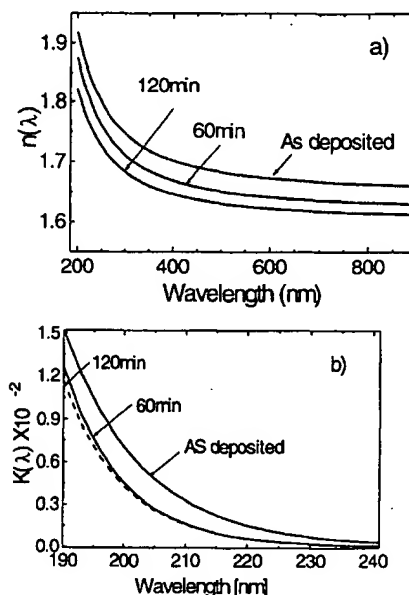


Fig. 3 a) Extracted  $n(\lambda)$  dependence from UV-VIS data by simulated spectra for as deposited sample and for annealed SiON films at 1050°C  
b)  $k(\lambda)$  dependence determined by fitting UV-VIS data with simulated spectra for as deposited sample and for annealed SiON films at 1050°C.

The extinction coefficient  $k$  at 190 nm decreases with about 21% after 2h of annealing. This means that the heating at 1050°C in wet oxygen determines an effect similar with the increasing in oxygen content in as-deposited LPCVD silicon oxynitride film clearly demonstrated in [12]. It requires a carefully measurement of the thickness variation of SiON film produced by annealing.

The discrepancy that remains after fitting between the calculated and experimental UV-VIS spectra is related mainly to non-homogeneous chemical in the silicon oxynitride film being the consequence of the assumed homogeneous layer approximation.

## V. CONCLUSIONS AND COMMENTS

Within this paper we have investigated the chemical changes in SiON films produced by both LPCVD conditions and by post annealing in a wet  $O_2$  atmosphere. The formation of a Si-O-Si bonds has been revealed as a time dependency from IR spectroscopic data.

We have found that the increase in Si-O-Si bonds population for annealing time longer than about 45 minutes at 1050°C is related to a diffusion limited chemical process. It is initiated by a low rate Si-O bond generation process, roughly estimated to be 21 time slower than the behavior at long time annealing. Also the increase in Si-O-Si bonds number as a result of high thermal annealing in wet oxygen has been indicated through the change of the refractive index by using a fitting approach based on the simulation of UV-VIS spectra.

The preliminary proposed model of the Si-O network formation at high temperature in

SiON films is based on the increased of oxygen incorporation through an diffusion limited reaction. This reaction is triggered by a previous structural change, produced by breaking Si-Si bonds in local  $Si[Si_2, A, H]$  tetrahedra, (where A can be N, OH,  $(NH)_2$ , or H). The OH group is considered the most probable molecular species to be involved in the tetrahedra oxidation. It is the best candidate for an enhanced diffusion coefficient, especially along the routes in SiON, populated with high density Si-O bonds.

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